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RAISELIFE

Raising the Lifetime of Functional Materials for Concentrated Solar Power Technology

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AR-Coating Abrasion Resistance Improvement and Selective Absorber Emittance Reduction Introducing aNew Infrared Reflector

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Executive Summary

AR-coatings (AR) developed by CIEMAT, with a solar transmittance of 0.975 and excellent resistance to outdoor exposition, present a moderate resistance to erosion and abrasion phenomena produced during cleaning procedure. AR porous silica layer is deposited on both glass surfaces by sol-gel deposition method using high withdrawal speed (40 cm/min) and it is currently used at industrial scale by two manufacturers of vacuum receiver tubes for parabolic trough collectors. Regarding selective absorbers, CIEMAT has also developed one with a solar absorptance of 0.955 and a thermal emittance of 0.13 at 250ºC, for linear focusing receivers.

Within RAISELIFE Project, and concretely in task 3.5, it was planned to extend and improve the optical properties and in-service life of receiver coatings. In fact, related to AR coating, many efforts have been applied to improve its mechanical resistance tested with a TABER abrasimeter. At this moment, mechanical resistance, considering number of strokes needed to remove coating, has been improved 2.5 times (from 40 to 100 strokes). Considering % of solar transmittance reduction after 10 strokes (where maximum transmittance losses are produced) the improvement is higher than 5 times (from 36 to 6%). Talking about the selective absorber, the efforts performed in this task have been focused in reducing the thermal emittance by adding an additional infrared reflector layer. Chromium, nickel and aluminium layers have been tested as infrared reflectors and chromium has revealed to provide better optical properties and higher thermal durability. Solar absorptance remains unchanged at 0.955 and thermal emittance at 250ºC is reduced from 0.13 to 0.09. Both stainless steel and chromium coated stainless steel absorbers have maintained optical properties after 18 months at 400ºC in air.

Table of Contents

2. Content of Deliverable

This deliverable contains the CIEMAT developments in the improvement of AR-coatings and selective absorber coatings for linear focussing solar receivers within RAISELIFE project. Main efforts have been subjected to improve abrasion resistance of AR-coatings to reduce damage produced during glass cover cleaning and reduction in thermal emittance of the absorber to increase receiver performance.

3. Results and Discussion

3.1. Antireflective coatings

AR-coatings for solar collector glass covers are composed of porous silicon dioxide and they are mainly deposited by sol-gel deposition technique because it is simple, inexpensive and moreover glass cover can be coated in both sides in a single step. Silicon dioxide has a refractive index very closed to glass and it is necessary to introduce porosity to decrease the refractive index in order to reduce reflective losses. This porosity presents the drawback of a reduction in mechanical properties and these AR-coatings are affected, during collector normal cleaning procedures, due to erosion and abrasion phenomena.

CIEMAT has developed and patented the use of a chemical compound, called Triton X-100, as a porogen compound [1]. Porogen materials are chemical compounds that introduce porosity in the material when sol-gel films are annealed. Increasing porogen concentration leads to an increase in porosity and antireflection effect. AR-coating developed by CIEMAT presents excellent optical properties with a solar transmittance of 0.975 in high quality borosilicate glass and good environmental resistance. Figure 1 shows the transmittance spectra of the AR coating developed by CIEMAT, measured with a Perkin-Elmer lambda 950 spectrophotometer. The measurements were obtained according to the standard ASTM E903-12 [2]. On the other hand, it is also noteworthy that the sol-gel precursor solution stability is quite large. It withstands fully operational more than five years when solution is used and maintained under controlled conditions of humidity and temperature. Colloidal commercial solutions used by other companies have a lifetime shorter than one year.

Within the framework of RAISELIFE project, the sol-gel precursor solution used to prepare the AR coatings has been improved, adjusting the porogen compound concentration in order to increase abrasion resistance without affecting the solar transmittance. Initial estimations were to improve abrasion resistance by the factor of 30 compared to the currently used coating. The current AR-coating presents a 35% reduction in transmittance after ten abrading cycles by using an abrader according MIL-B-12397 and it is completely removed after 40 abrading cycles. Improved AR-coating has a 6% reduction in solar transmittance after 10 cycles and it withstand 100 cycles.

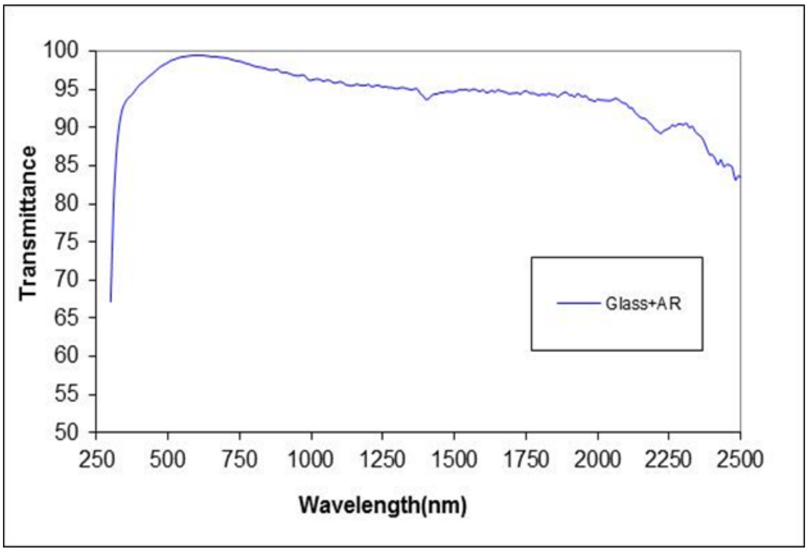

Figure 1: spectral transmittance of AR-coating developed at CIEMAT

In order to improve AR-coating abrasion resistance, porogen content has been optimized. Several precursor solutions were prepared with different porogen content and solar transmittance values obtained were analysed. Transmittance spectra of samples prepared with different porogen concentration are shown in Figure 2. It can be appreciated that there is no difference in the spectra of samples prepared with 1.5 and 2g/l. Then, the porogen content can be reduced from actual 2 g/l content to 1.5 g/l without affecting the optical performance.

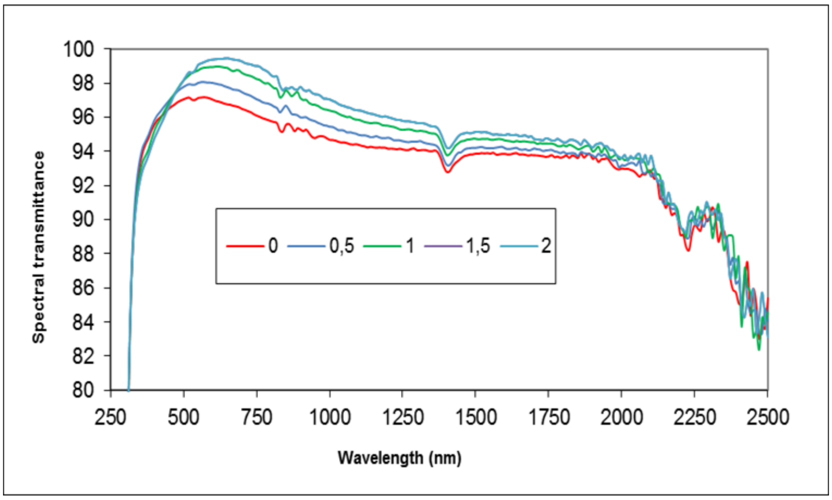

Figure 2: Spectral transmittance of AR-coating prepared with different Triton X-100 content.

Another parameter investigated is solution aging. Usually, Triton X-100 is added the day after solution preparation and precursor solution is ready to be used. Regarding this issue, different solution aging times before adding the porogen compound were tested. The results showed that adding this compound four days after solution preparation leads to an improvement in coating mechanical properties. This phenomenon is produced because porogen reduces solution polymerization and after four days a denser network is obtained if porogen is not present at the beginning.

In order to check mechanical properties of AR-coatings, quantitative standard test are not available yet and a qualitative tests such as Taber abrasion test which is the test foreseen in draft of international standard IEC 62862-3-3[3 is used here to evaluate abrasion resistance of glass tubes. In this test, an abrader is moved on the surface of the AR-coating with a controlled speed and transmittance is measured periodically after several cycles to check when the coating is completely removed. The test conditions are summarized next:

. Equipment: TABER linear abraser model 5750

· Load weight: 350 gr.

· Length: 38.1mm (1.5 inches).

. Speed: 7 cycles/min

· Abrasive material: According to MIL-12397, 6mm diameter.

· Ambient conditions.

In figure 3, the solar transmittance values variation with the number of cycles is presented for older solution and the new one with lower porogen content.

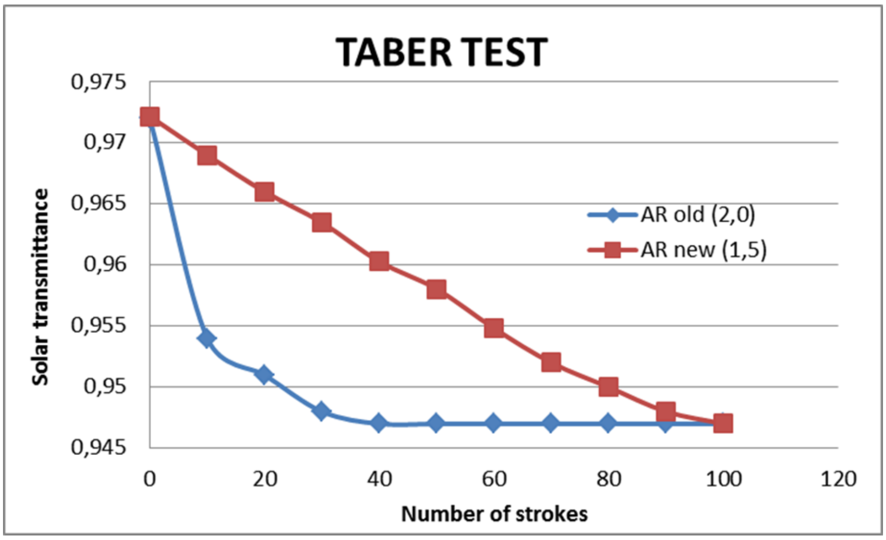

Figure 3: Taber abrasion test results

It should be note that the new solution produces a strong improvement in mechanical properties and coating abrasion is nearly linear. With older solution, more than 70% of antireflection effect (considering only outer layer) is lost after 10 cycles. With the new one, this loss is only 12%, so it means that a relative improvement of 6 times is obtained. If it is considered the number of cycles necessary to remove completely the AR- coating, the improvement rises from 40 to 100 cycles and a relative improvement of 2.5 times is obtained with the new solution.

In table 1, the solar transmittance values and transmittance reduction percentage are presented against number of abrasion cycles. Reduction percentage is calculated considering the antireflective effect of one side AR-coating layer. At the beginning, solar transmittance is 0.972 and when one side is removed by the abrader is 0.947.

Table 1: Solar transmittance values and reduction percentage during Taber abrasion test for old and new solution.

Cycles	Old AR (2.0g/l)	% reduction	New AR (1.5g/l)	% reduction
0	0.972	-	0.972	-
10	0.954	72	0.969	12
20	0.951	84	0.966	25
30	0.948	96	0.963	35
40	0.947	**100**	0.960	47
50	0.947	100	0.958	56
60	0.947	100	0.955	69
70	0.947	100	0.952	80
80	0.947	100	0.950	88
90	0.947	100	0.948	96
100	0.947	100	0.947	**100**

AR-coating developed by CIEMAT presents an excellent outdoor durability and, in order to check that the variations tested in the solution have not affected this durability performance, three ARC samples, prepared with 1.5 g/l of Triton X-100, has been tested at a temperature of 85ºC and an humidity of 85%, according to the Damp-heat test usually performed for anti-reflective coatings. Solar transmittance values obtained during the test time are shown in figure 4. It can be appreciate that excellent results were obtained, with only a small decrease in solar transmittance during the test.

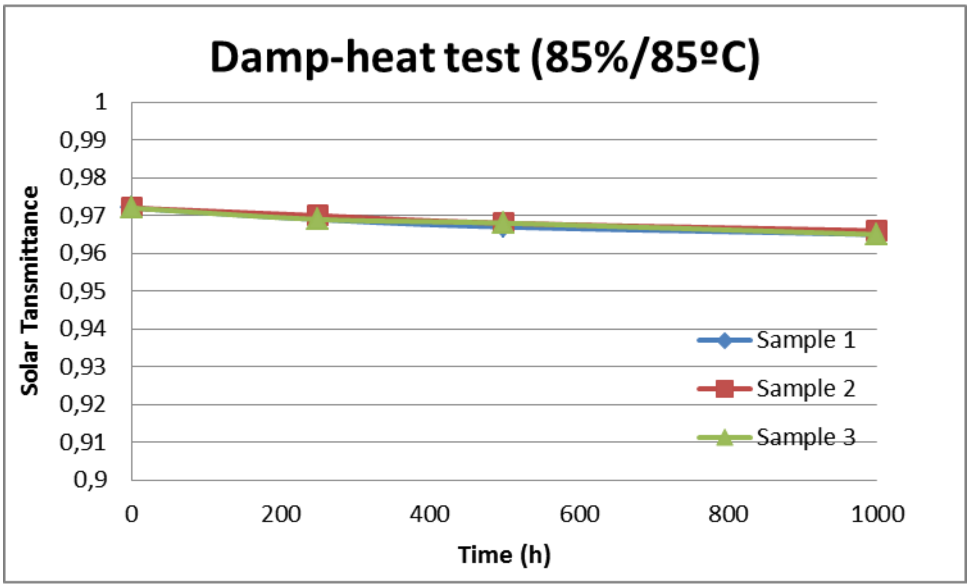

Figure 4: Solar transmittance of ARC samples (1.5 g/l) tested at 85ºC and 85% humidity in a weathering chamber

It is important to highlight that the changes produced on precursor solution composition or preparation method are minimal and they do not affect deposition parameters of the coatings or solution stability. This implies that new solution can be used directly at industrial scale to replace the older one, without any change in factory facilities (solution preparation or deposition system) and solution lifetime will be similar than older one.

3.2. Selective absorbers

CIEMAT has developed a selective absorber on AISI 316 stainless steel (SS), composed of a spinel absorbing layer [4] and a silicon dioxide AR layer, with a solar absorptance of 0.955 and a thermal emittance at 250ºC of 0.13. The reflectance spectrum of this absorber is recorded in Figure 5, and it is stable in air at temperatures higher than 350ºC. Within WP 3.5 of RAISELIFE project the main objective related to selective absorbers for linear focusing receivers, is to reduce thermal emittance for increasing efficiency of solar thermal applications.

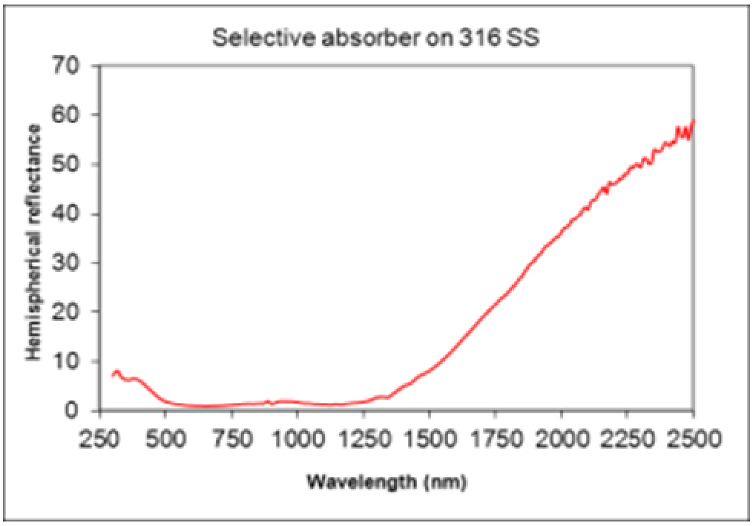

Figure 5: Hemispherical reflectance of selective absorber developed at CIEMAT.

Within this task, several additional infrared reflectors have been checked (nickel, chromium and aluminium) in order to reduce thermal emittance. Nickel and chromium were electrodeposited on stainless steel whereas the aluminium infrared reflector was a composite tube with a SS core tube and with an external aluminium tube. This composite tube had a diameter of only 20 mm and it could not be properly measured. In figure 6, the complete hemispherical reflectance spectra of SS, and Cr and Ni deposited SS tubes are shown.

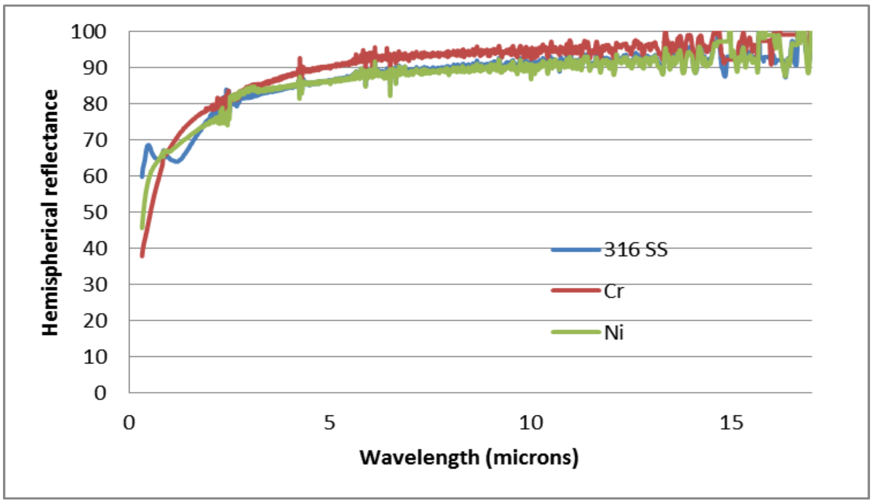

Figure 6: Hemispherical reflectance of different IR reflectors tested.

Thermal emittance was calculated at 250°C for the different IR reflectors, and the results are recorded in Table 2.

Table 2: thermal emittance at 250°C of different absorbers prepared.

Material	Emittance (250ºC)
316 SS	0.105
Cr	0.069
Ni	0.104

The thermal emittance values of 316 SS and Cr are in accordance with the values referred in the literature but the value obtained for Ni is too high, approximately double the actual value. This means that nickel coating has not enough purity or that additives used in electrodeposition baths have been incorporated in the coating. So, further development has been focused on stainless steel and chromium coated stainless steel.

The preparation of the selective absorber is made by dip coating. In this technology, the precursor solution is applied on the substrate by immersion and after that the sample needs to be cured at temperatures higher than 450°C for coating annealing. Therefore, the substrate or infrared reflector layer has to withstand this thermal treatment without strong oxidation in order to tailor the interference effects to produce a selective behaviour. If strong oxidation is produced, optical interferences move to longer wavelengths and it is not possible to make a good selective absorber. Chromium and 316 SS substrates were heated at 500°C, during 1 hour, to check the extent of the oxidation process. In figures 7 and 8 it can be seen the hemispherical reflectance spectra, before and after oxidation, for 316 SS and Cr.

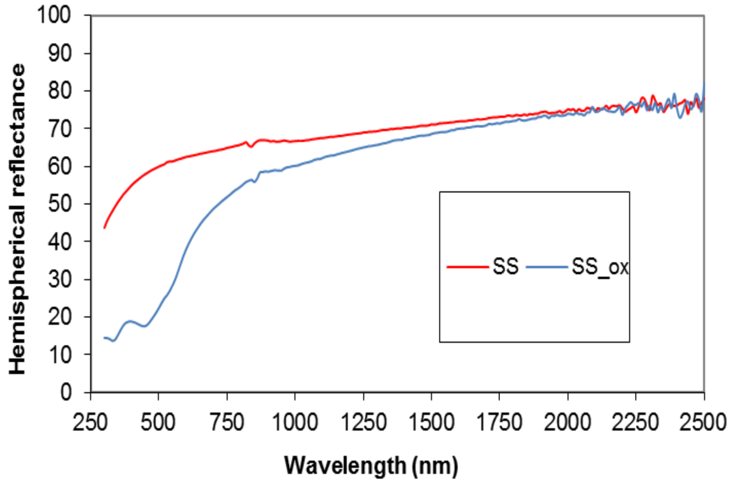

Figure 7: 316 SS hemispherical reflectance before and after thermal treatment..

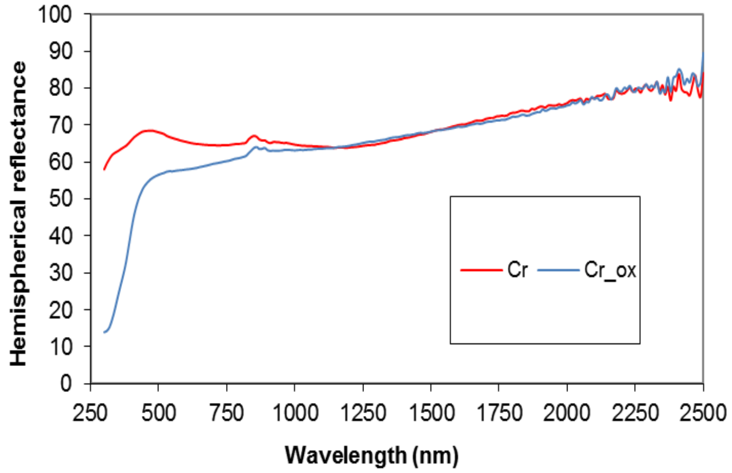

Figure 8: Chromium hemispherical reflectance before and after thermal treatment..

It can be seen for 316 SS and chromium that hemispherical reflectance is affected only in UV and visible spectra, suggesting this, the formation of a thin oxide film on the substrate. Thus, it can be said that it is possible to use both material as infrared reflector in this selective absorbers.

In figure 9, hemispherical reflectance of the absorber prepared on chromium plated steel is shown. This absorber has a solar absorptance of 0.954 and a thermal emittance at 250ºC of 0.093. In the next months, more chromium plated pipes will be received to optimize both layer thickness and reduce thermal emittance as much as possible.

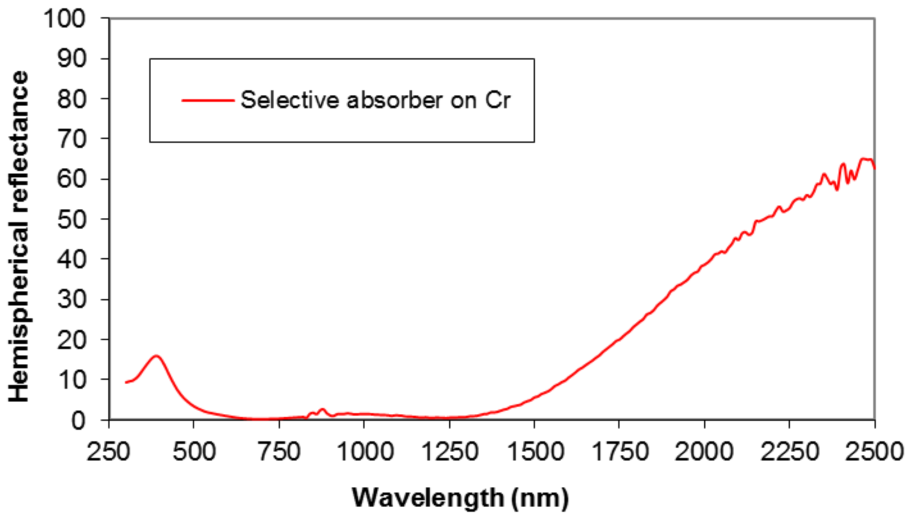

Figure 9: hemispherical reflectance of selective absorber chromium plated substrate.

Regarding aluminium composite pipe, it was not possible to measure optical properties due to the small pipe diameter, but final coating prepared on it, is dark blue with a similar visual appearance than coatings prepared on flat aluminium samples. Larger diameter pipes are expected to be received within the next months to measure optical properties and optimize coating on these substrates.

In figure 10, the hemispherical reflectance of a three layer absorber [5] on aluminium is presented, with a solar absorptance value of 0.955 and a thermal emittance value of 0.05 at 250ºC.

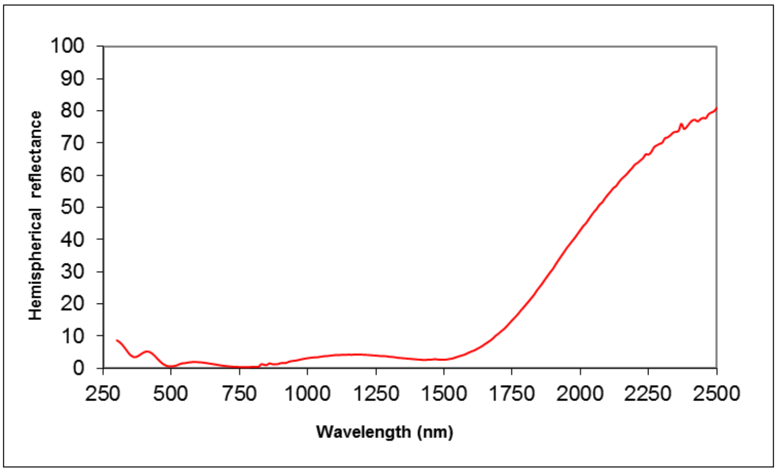

Figure 10: Hemispherical reflectance of selective absorber deposited on a flat aluminium IR reflector.

In order to summarize the selective absorber results, optical properties of bare and coated different infrared reflectors are shown in table3.

Table 3: Optical values of selective absorbers tested.

	Uncoated	Selective absorber	
Substrate	$\varepsilon_{250ºC}$	$\varepsilon_{250ºC}$	**α**
316 SS	0.105	0.130	0.955
Cr	0.069	0.093	0.954
Al	0.030	0.050	0.955

During the project time, selective absorber durability tests have been also performed. At the beginning of the project, thermal durability of stainless steel and chromium coated stainless steel samples were studied at 300ºC and 350ºC showing no degradation. In view of these results, temperature was increased up to 400ºC. After 15 months at 400C in air, both selective absorbers have not shown any degradation in optical properties or layer adhesion. In table 4 and 5, optical properties of stainless steel (SS) and chromium coated stainless steel (Cr-SS), before and after 15 months at 400ºC, are shown.

Table 4: Optical properties of stainless steel selective absorber before and after 15 months in air at 400ºC

	Initial	*After 15 months at 400C*
Solar absorptance	0.951	0.951
Thermal emittance (250C)	0.133	0.133

Table 5: Optical properties of chromium coated stainless steel selective absorber before and after 15 months in air at 400ºC

	Initial	*After 15 months at 400C*
Solar absorptance	0.954	0.956
Thermal emittance (250C)	0.087	0.091

From the results showed in table 4, it is clear that the thermal stability of the selective absorber deposited on stainless steel tube is excellent without changes in solar absorptance and thermal emittance values, showing that absorber and antireflective layers together with the native stainless steel oxide layer are able to protect stainless steel against thermal oxidation at 400ºC. In figure 11 and 12, spectral hemispherical reflectance, in solar and IR spectral regions, are shown for SS absorber before and after test.

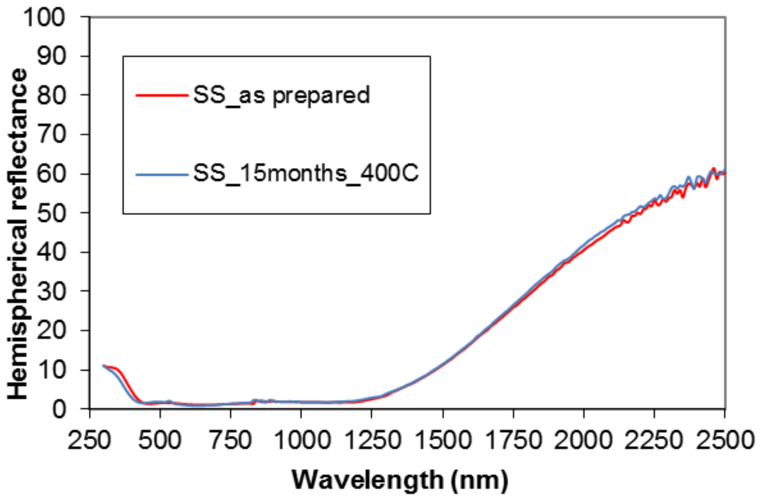

Figure 11: Solar Hemispherical reflectance of SS absorber before and after 15 months at 400ºC.

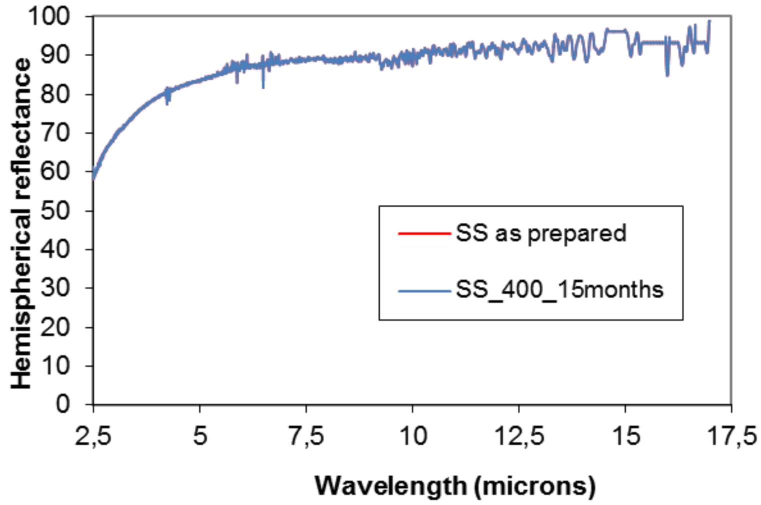

Figure 12: IR Hemispherical reflectance of SS absorber before and after 15 months at 400ºC.

Regarding the values shown in table 5, there is a slight change in optical properties, with a small increase in the solar absorptance value from 0.954 to 0.956 and an increase in thermal emittance from 0.087 to 0.091, too. In figure 13 and 14 the spectral hemispherical reflectance, in solar and IR spectral regions, for Cr-SS absorber before and after test are shown.

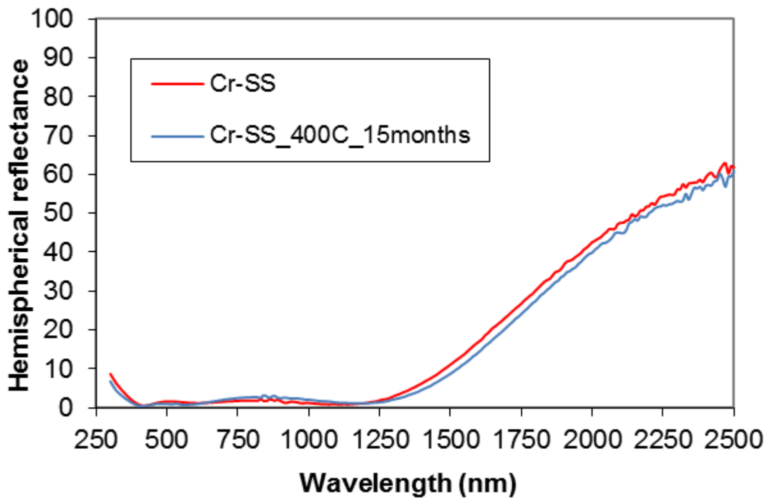

Figure 13: Solar Hemispherical reflectance of Cr-SS absorber before and after 15 months at 400ºC.

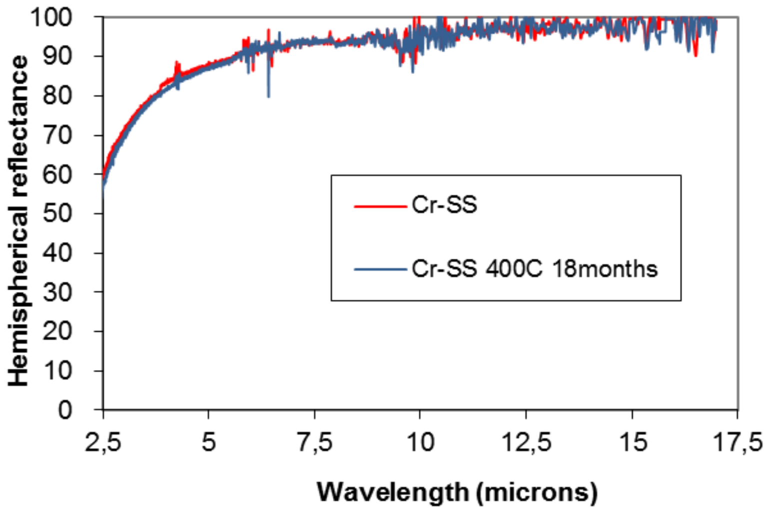

Figure 14: IR Hemispherical reflectance of Cr-SS absorber before and after 15 months at 400ºC.

In figure 13, it can be seen that there is a small change in the absorber reflectance that is attributed to a slight oxidation of the chromium infrared reflector that produces an increase in both solar absorptance and thermal emittance values. These variations do not have any influence in solar receiver performance due to their small magnitude and that operation temperature of these solar collectors is not so high.

Considering that both stainless steel and chromium coated stainless steel absorbers do not show degradation at 400ºC, samples are now being tested at 450C in air.

Finally, the most promising selective absorber developed, that uses additional chromium infrared reflector layer, has been optimized in order to reduce thermal emittance by adjusting the absorbing and antireflective layer thicknesses. This optimization gives place to a solar absorptance value of 0.954 and a thermal emittance of 0.078 at 250ºC In figure 15 and 16 the spectral hemispherical reflectance for Cr-SS absorber with theoptimized thicknesses, in solar and IR spectral regions respectively are shown .

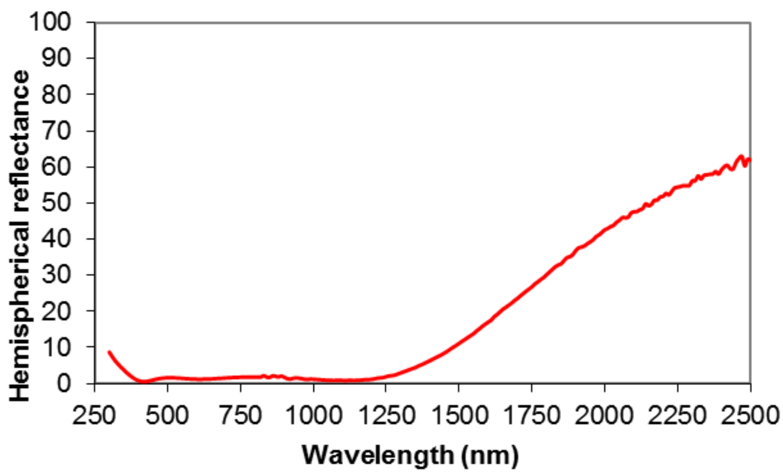

Figure 15: Solar Hemispherical reflectance of Cr-SS absorber.

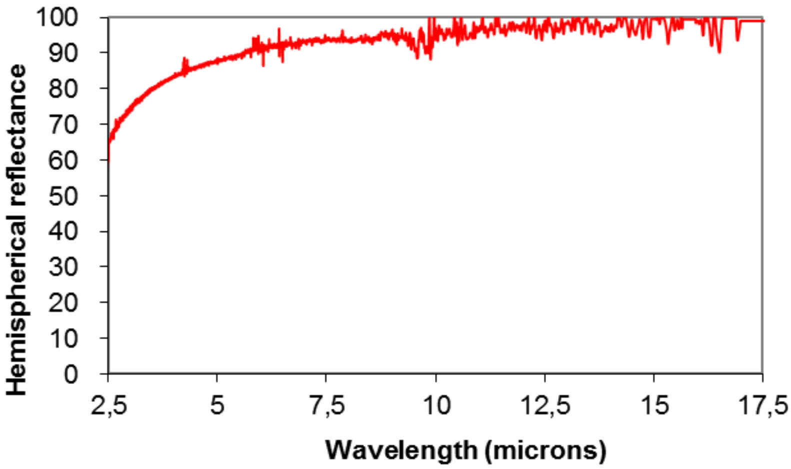

Figure 16: IR Hemispherical reflectance of Cr-SS.

Thermal emittance final value obtained with the optimized absorber on chromium coated stainless steel is 0.078 that is under value targeted at the beginning of the project (0.08). Thermal durability tests performed during 15 months at 400ºC with no degradation proves that the developed absorber will be stable at 250ºC during normal lifetime in a commercial solar plant.

4. Conclusions

Antireflective coatings prepared by CIEMAT have been optimized in order to improve mechanical properties. Precursor solution composition and preparation method have been slightly modified and a relative improvement factor of 6 has been obtained in abrasion Taber test results. After 10 abrasion cycles, transmittance losses has been reduced from 72% to 12% with the new solution composition. Solution changes do not affect deposition parameters or solution stability, so new solution can be used at industrial scale without additional requirements.

Two different additional infrared reflector layers have been tested to reduce emittance of the absorber developed by CIEMAT. Nickel infrared reflectors did not withstand absorber annealing conditions and it was neglected. Chromium reflective layer, produced by electrodeposition, presented excellent results, with a solar absorptance of 0.954 and a thermal emittance at 250ºC as low as 0.078. Thermal stability at 250ºC has been proven because thermal durability tests, performed at 400ºC during 15 months, did not show any degradation in the absorber.

5. Degree of Progress

Antireflective coating sol-gel precursor solution has been improved, adjusting porogen compound concentration used to promote porosity, in order to increase abrasion resistance without affecting the solar transmittance. It was estimated to obtain an improved abrasion resistance by the factor of 30 compared to the currently used coating in the FRESH NRG project and real improvement achieved has been around 6. Losses in transmittance have been dramatically reduced at lower abrading cycles according to MIL-B-12397 and the new one withstands 100 cycles before layer removal. Therefore, project objectives regarding increasing AR-coating mechanical properties have not completely fulfilled but a strong improvement has been produced anyway.

Thermal emittance final value obtained with the optimized absorber on chromium coated stainless steel is 0.078, which is under value targeted at the beginning of the project (0.08). Thermal durability tests performed during 15 months at 400ºC with no degradation proves that developed absorber will be stable at 250ºC during normal lifetime in a commercial solar plant.

6. Dissemination Level

7. References

[1] Morales A.; 2001; "Sol-gel process to the preparation of porous coatings, using precursor solutions prepared by polymeric reactions"; EP 1329433

[2] Standard Test Method for Solar Absorptance, Reflectance, and Transmittance of Material Using Integrating Spheres, ASTM E903-12.

[3] Draft standard IEC 62862-3-3: Solar thermal electric plants – Part 3-3: Systems and components – General requirements and test methods for solar receivers.

[4] Morales A.; 2001; "Process to deposit metal and metal oxides"; EP 1321539

[5] Farchado M.; Rodríguez, J.M.; Morales, A., San Vicente, G.; "Optical parameters of a novel competitive selective absorber for low temperature solar thermal applications"; Solar Energy Materials and Solar Cells 178 (2018) 234-239.

8. Appendix